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Comparison of Chromatographic Data from Corner Express **Texaco and Priceless Gas Sites**

April 16, 2003

Comparison of Chromatographic Data for Product and Groundwater Samples at the Priceless Gas Site

The Basis for Comparison were as Follows:

- 1) Overall Chromatographic pattern. All samples were analyzed using Agilent GCs equipped with high performance capillary columns and combination FID/PID detectors. The patterns from both detectors were examined and used for comparison. Copies of the PID chromatograms that have been scaled to the highest peak have been provided.
- 2) Presence or absence of MTBE and relative concentrations.
- 3) Ratios of key aromatic compounds. Concentrations of Benzene to Toluene (B/T), Toluene to Xylenes (T/X) and Benzene plus Toluene to Ethylbenzene plus Xylenes were used to develop the ratios.

Discussion of Relevant Factors Related to Basis for Comparison:

1) a. Pattern Analysis

The presence or absence of characteristic peaks and their relationship to one another form the basis for pattern analysis. GC chromatograms are essentially "snap shots" of the hydocarbons present. Comparison of these "pictures" attempt to answer the question whether A and B are similar to each other or not similar to each other and if they are similar are they exact matches.

1) b. Weathering Characteristics

Weathering of Gasoline products in nature occurs mostly through loss of the most volatile compounds preferentially to less volatile compounds due to evaporation or dissolution. An absence of or decrease in area counts for compounds occurring in the chromatographic pattern before Toluene when compared to a "fresh" Gasoline standard is the best indication that weathering has occurred.

Judgements vary from "slight" to "severe" weathering depending upon whether the most volatile compounds have moderate decreases in area count or are lost from the pattern.

2) MTBE

MTBE was confirmed at very high concentrations in water samples from the Priceless Gas site. This compound can be used as a "marker" when comparing results from different sources.

3) Ratios of Key Aromatic Compounds

Overall pattern analysis is a subjective measure. In order to create a basis for a more objective comparison of Gasoline chromatograms the ratios of the concentrations of key Aromatic compounds were calculated and compared. The BTEX ratio results have been summarized in the attached "Table of Relevant Factors for Comparison".

a. Benzene plusToluene to Ethylbenzene plus Xylene (B+T/E+X) Ratio This composite ratio has been used in the current literature as an indicator of weathering. The ratio decreases with increased aging due to the preferential loss of the more volatile and dissolvable Benzene and Toluene compounds. It is useful for purposes of this report to differentiate sources of hydrocarbon contamination through comparison of the ratios of products from various sources to each other. A general statement related to aging of the source is also possible.

b. Benzene to Toluene (B/T) Ratio

This ratio is relatively constant within the grade of gasoline from source to source. That is, the ratio for unleaded gasoline is typically 1 to 3. The ratio can change dramatically, however, from grade to grade because of the blending of aromatic fractions containing high concentrations of Toluene or Benzene that occurs at the refinery or blending facility. Premium gasoline and aviation gasoline for instance contains relatively higher concentrations of Toluene than would be found in Unleaded regular gasoline. This ratio then is most useful when differentiating sources that are impacted by different grades or types of gasoline.

b. Toluene to Xylenes (T/X)

The (T/X) ratio is not as vulnerable to changes due to weathering as the (B/T) ratio since Toluene is more environmentally stable than Benzene. The ratio is also useful in differentiating sources by grade since the relative concentration of Toluene varies by grade.

Evaluation of Gasoline Sources

Dissolved Gasoline/BTEX, MTBE results were examined for three reference gasoline product samples and seven well samples taken in February 2003.

The following is a discussion of the various sources as they relate to each other and to the reference gasoline products using gas pattern and BTEX ratio analysis.

Priceless MW-1

- 1) The chromatographic pattern was not characteristic of a typical gasoline. In fact the pattern was more characteristic of a gasoline additive than a finished gasoline. The hydrocarbon present is predominantly a mixture of Benzene and MTBE along with a minor amount of typical gasoline compounds. I have called this the "Priceless" pattern in the comparison table.
- 2) There was a very high concentration of MTBE present in the sample (44% when compared to total gasoline range components).
- 3) The (B/T) ratio was 55.2 meaning there was 55 times more Benzene present than Toluene.
- 4) The (T/X) ratio was 0.4 or 1:3 which is consistent with the free product samples of unleaded gasoline. One possibility for these ratios is that the product in the water may be an octane booster package of Benzene, MTBE and other oxygenates or light-end components in association with a small amount of unleaded gasoline.

Priceless MW-2

- 1) The overall pattern was very similar to that found in MW-1, however, there is more of the typical gasoline components present in this well than in MW-1. The pattern is best described as a mixture of Priceless with unleaded gasoline.
- 2) There was a very high concentration of MTBE present in the sample (8.2% when compared to total gasoline range components).
- 3) The (B/T) ratio was 6.5 meaning there was 6.5 times more Benzene present than Toluene.
- 4) The (T/X) ratio was 0.14 or 1:7 which is consistent with the free product samples of unleaded gasoline. One possibility for these ratios is that the product in the water may be an octane booster package of Benzene, MTBE and other oxygenates or light-end components in association with a small amount of unleaded gasoline.

The T/X ratio is also consistent with the product taken from well MW-3a.

Texaco MW-5

- 1) The overall pattern was a strong match with a typical unleaded gasoline pattern. The pattern was a closer match to that for the product from well MW-3a than either of the unleaded dispenser products. It was not a match for either the Premium grade or the Priceless patterns.
- 2) MTBE was not present in significant concentration in the sample (1.5% of total gasoline range components, unconfirmed).
- 3) The (B+T/E+X) was 0.2 which indicates possible aging when compared to the product samples which were 0.8 to 0.9.
- 4) The (B/T) ratio at 3.1 was consistent with the unleaded gasoline product samples at 2-3.5.

 The (T/X) ratio was also typical of an unleaded gasoline that had been aged and therefore lost Toluene preferentially to Xylenes. The ratio was a very good match with the product sample taken from the sorbant material in MW-3a.

Texaco MW-30

- 1) The overall pattern is the same as that found in well MW-5.
- 2) MTBE was not present in significant concentration in the sample (1.43% of total gasoline range components, unconfirmed.
- 3) The (B+T/E+X) ratio is 0.4 which is consistent with an unleaded gasoline that has been aged. The ratio was a match with the product in well MW-3a and similar to the ratio for MW-5.
- 4) The (B/T) ratio at 3.2 was consistent with the unleaded gasoline product samples and a match to the ratio for MW-5. The (T/X) ratio was also typical of an unleaded gasoline that had been aged and therefore lost Toluene preferentially to Xylenes.

Product Samples from MW-3a

1) The overall patterns for both samples are consistent with an unleaded gasoline. Both patterns show signs of slight weathering (aging) when compared to patterns of fresh product. The pattern for the sorbant material shows slightly more signs of aging than the product sample. The pattern is not consistent with the Priceless pattern. The pattern is similar to but not identical with the pattern for the dispenser products.

- 2) MTBE was not present in significant concentrations in either sample.
- 3) The BTEX ratios for both products were consistent with an unleaded gasoline product that had been slightly weathered. The ratios indicate that the Sorbant material was more weathered than the product sample.

Product Samples from the East and West Dispensers

- 1) The overall patterns for both samples are consistent with unleaded gasoline. The patterns are identical to each other indicating that they are the same product.
- 2) MTBE was not present in significant concentrations in either sample.
- 3) The BTEX ratios for both products were consistent with unleaded gasoline. Neither pattern was remotely similar to the Priceless pattern.

Premium Gas Sample

- 1) The overall pattern for the sample is similar to the unleaded gas patterns but dominated by Toluene. Toluene is the single largest component in the pattern.
- 2) MTBE was not present in significant concentrations in either sample.
- 3) The BTEX ratios are different than all others because of the high Toluene concentration.

Conclusions

- 1) The chromatographic patterns for Gasoline contamination found in groundwater from wells on the Priceless Gas site is significantly different from that found in wells on the Corner Texaco site.
- 2) The product in well MW-3a is a weathered unleaded gasoline and a very close match with the contamination in Texaco wells MW-5 and MW-30.
- 3) The Pattern for the Premium gas is significantly different from the unleaded pattern and is not repeated in any of the monitoring wells.

- 4) Because of the lack of MTBE in significant concentrations, the groundwater in the Corner Texaco site does not seem to have been impacted by contamination from the Priceless Gas site.
- 5) The gasoline range contaminant in Priceless well MW-1 is a mixture of Benzene, MTBE and perhaps another oxygenate. Its pattern is more consistent with a fuel additive than a finished fuel. Priceless Well MW-2 has a more complicated pattern of contamination than well MW-1.

It should be noted that the above comparisons were performed using GC chromatographic equipment and conditions designed for hydrocarbon screening analysis and by no means represent a definitive study of hydrocarbon contamination on either site.

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